Internal Rotation in n-Propyl Chloride and Bromide

By Chizuko KOMAKI, Isao ICHISHIMA, Kenji KURATANI, Tatsuo MIYAZAWA, Takehiko SHIMANOUCHI, and San-ichiro MIZUSHIMA

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Introduction

In a previous paper it was shown by the Raman measurement that *n*-propyl halides exist in two forms in the liquid state and in only one form in the crystalline state.[1] The same conclusion was drawn by Brown and Sheppard[2] from their infrared absorption measurement of *n*-propyl bromide. Goubeau and Pajenkamp have reported the energy difference between the rotational isomers of *n*-propyl chloride and *n*-propyl bromide[3]. However, as the stable molecular forms have not yet been determined, we have made further spectroscopic studies of these substances. The results will be reported in the present paper.

Vibrational Spectra

The sample used in the measurement was prepared from *n*-propyl alcohol and phosphorous trihalide and purified by distillation under ordinary pressure using a column having 30 theoretical plates. The materials used were center fraction boiling over a range of ±0.1°C. Raman spectra were measured with the spectrograph of our own construction[4] and the infrared absorptions with the Baird spectrophotometer with the NaCl and KBr prisms. The results are listed in Tables I and II. In these tables are also shown

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[1] S. Mizushima, Y. Morino and S. Nakamura, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **37**, 205 (1940).

[2] J.K. Brown and N. Sheppard, *Disc. Faraday Soc.*, **9**, 144 (1950).

[3] J. Goubeau and H. Pajenkamp, *Acta Physica Austriaca*, **3**, 283 (1949).

[4] S. Mizushima, "Structure of Molecules and Interna Rotation," Academic Press, New York (1954).

TABLE I

RAMAN AND INFRARED FREQUENCIES OF $CH_3CH_2CH_2Cl$

Observed					Calculated		
Gas	Liquid		Solid		*trans*	*gauche*	Type of Vibration
I. R.	I. R.	R.	I. R.	R.[1]			
		144 (2b)					
		220 (0b)					
		249 (2b)		229 (1)	252		δ *trans*
		292 (3)		——		267	δ *gauche*
		368 (6)		363 (5)	334		δ *trans*
	426 (m)	426 (4)		——		429	δ *gauche*
660 (s)	648 (s)	651 (8)	——	——		708	ν (C-Cl) *gauche*
			700 (w)				
743 (s)	729 (s)	728 (6b)	717 725 (s)	716 (7)	744		ν (C-Cl) *trans*
	749 (m)	——	749 (s)				CH_2 *rocking* *trans*
787 793 800 (s)	789 (s)	788 (6)	——	——			CH_2 *rocking* *gauche*
852 858 864 (s)	856 (s)	856 (4)	863 (m)				
894 903 (s)	897 (s)	896 (3)	898 (s)				
1038 (m)	1034 (s)	1026 (6)	1030 (m)	1029 (5)			
1050 (m)	1067 (m)	1064 (1)	1065 (w)				
1067 (w)	1081 (w)	1088 (0)	1083 (m)				
1097 (w)	1094 (w)						
	1104 (w)	1108 (1)	1103 (w)				
	1158 (w)		1155 (vw)				
	1213 (w)	1211 (1)	1218 (vw)				
1253 1261 (s)	1258 (s)	1255 (2)	1257 (s)				
1300 1309 (s)	1304 (s)	1297 (1)	1287 (vw)				
1331 (m)	1338 (m)	1341 (3)	1332 (m)				
1390 (m)	1385 (s)	1381 (0)	1370 (m)				
1456 (s)	1447 (s) 1460 (s)	1441 (5) 1462 (2b)	1460 (s)	1441 (2)			
		2743 (4)					
		2854 (2)		2829 (0)			
2870 (s)		2876 (6)		2870 (5)			
	2900 (s)	2900 (3b)		2894 (2)			
		2915 (3b)		2908 (2)			
		2936 (6)		2941 (6)			
2950 (s)	2960 (s)	2957 (6)					
		2979 (3)		2975 (0)			
		3003 (3)		2997 (0)			

1. Frequencies reported in reference 1).

the infrared absorption spectra in the crystalline state observed in the frequency range 600 to 800 cm.$^{-1}$ with the use of a spectrophotometer of our own construction4).

Rotational Isomers

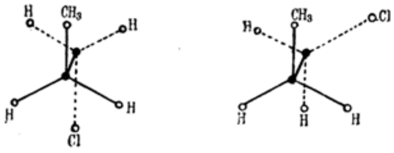
As has been shown in many of our previous papers on internal rotation, the absence of some of the liquid spectral lines in the solid state (Tables I and II) shows the presence of rotational isomers in the liquid state1). In the solid state, however, the presence of only one isomer is sufficient to account for the number of the observed lines.

TABLE II

INFRARED FREQUENCIES OF $CH_3CH_2CH_2Br$

Gas	Liquid	Solid	Type of Vibration
	406		
561 (s)	564 (s)		ν(C-Br) *gauche*
658 (s)	646 (s)	638 (s)	ν(C-Br) *trans*
742 (w)	741 (m)	737 (s)	CH_2 *rocking trans*
775 780 785 (s)	777 (s)	——	CH_2 *rocking gauche*
837 (s)	838 (s)	849 (w)	
892 (s)	887 893 (s)	892 (s)	
1033 (s)	1030 (s)	1025 (m)	
1085 (m)	1079 (m)	1038 (s)	
	1094 (w)	1099 (m)	
	1196 (m)		
1232 (s)	1225 (s)	1218 (s)	
1290 (s)	1284 (s)	——	
1339 1351 (m)	1326 1340 (m)	1321 (s)	
1391 (s)	1381 (s)	1364 (s)	
1456 (s)	1437 1460 (s)	1445 (s)	
2900 (s)	2890 (s)		
2960 (s)	2960 (s)		

We are now interested in determining the molecular configurations of the rotational isomers. The symmetry considerations cannot be applied conveniently for this molecule. However, from the nature of the hindering potential discussed in a previous paper[5], the stable configurations of this molecule can be considered to be the *trans* and *gauche* forms shown in Fig. 1. Accordingly the normal vibration calculation of the skeleton $(CH_3)\cdot(CH_2)\cdot(CH_2)\cdot Cl$ has been made for the *trans* and *gauche* forms according to the method described in a previous paper[6]. The force constants used in this calculation are those which yielded the computed frequency values in good agreement with those observed for other molecules with similar structure.



Trans form *Gauche* form

Fig. 1. Stable molecular configurations of *n*-propyl chloride.

The computed skeletal frequencies of *n*-propyl chloride are shown in Table I. Those for the *trans* form are close to the frequencies observed in the solid state. Accordingly we conclude the stable configuration in the solid state to be the *trans* form, in which the CH_3 group and the Cl atom are farthest apart. The fact that all the solid frequencies are also observed in the liquid state shows that the *trans* form is one of the stable configurations in this state. The other stable configuration can be considered to be the *gauche* form, since the Raman lines observed only in the liquid state have frequencies close to those calculated for the *gauche* form.

In order to confirm this conclusion, we have calculated the dependence of the skeletal deformation frequency on the azimuthal angle θ of internal rotation, because this frequency is very sensitive to the change of this angle[6] and accordingly we can determine fairly accurately the azimuthal angle from the observed frequency value. The result of this calculation is shown in Fig. 2, from which we see that the observed frequencies are close to those calculated for the *trans* ($\theta=180°$) and the *gauche* ($\theta=60°$) forms, respectively.

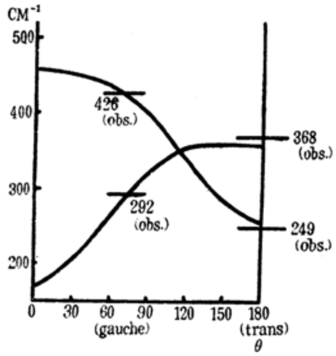


Fig. 2. Dependence of skeletal deformation frequencies on azimuthal angle.

The conclusion was also checked by the product rule derived in our previous paper[6]. If we denote the kinetic energy matrices for the *trans* and *gauche* forms by G_t and G_g, respectively, we have

$$(|G_g|/|G_t|)^{\frac{1}{2}}=\Pi\nu_g/\Pi\nu_t \qquad (1)$$

where ν_t and ν_g are the normal frequencies of the *trans* and the *gauche* molecules. The ratio on the left-hand side of this equation has been calculated as the function of θ as shown in Fig. 3, putting θ of the *trans* form as 180°. The experimental value $\Pi\nu_g/\Pi\nu_t$ is close to that calculated for the *gauche* form ($\theta=60°$).

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[5] S. Mizushima, Y. Morino and T. Shimanouchi, *J. Phys. Chem.*, 56, 324 (1952).

[6] S. Mizushima, T. Shimanouchi, I. Nakagawa and A. Miyake, *J. Chem. Phys.*, 21, 215 (1953).

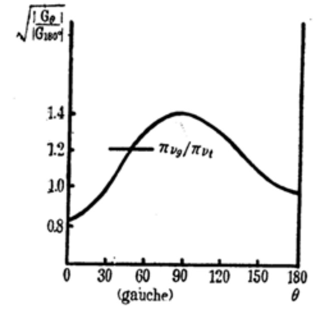

Fig. 3. The calculated values of $(|G_\theta|/|G_{180°}|)^{1/2}$ and the observed value of $\Pi\nu_g/\Pi\nu_t$.

In addition to the confirmations made by these calculations we have an experimental evidence in support of the assignment of lines made above. n-Propyl chloride has a chain structure similar to that of ethylene chlorhydrin so that the skeletal frequencies of these two molecules will not be very different from each other. Actually these two substances show similar low frequency lines in the liquid and the gaseous states. However, there is a great difference between the spectra of these two substances in the solid state. Namely, the lines 292, 426, 651 cm.$^{-1}$ of liquid n-propyl chloride disappear on solidification, whereas the corresponding lines of ethylene chlorhydrin persist in the solid state. From this we can conclude that the configuration of n-propyl chloride in the solid state must be different from that of the crystalline ethylene chlorhydrin. Now that our previous measurement[7] has shown the *gauche* form to be present in the crystalline state of ethylene chlorhydrin, we can conclude that the molecule of n-propyl chloride in the solid state is the *trans* form in conformity with the conclusion drawn from the normal vibration calculation.

Energy Difference between the Rotational Isomers

The energy difference between the rotational isomers has been determined by the measurement of the ratio of optical densities D of the two infrared absorption bands, one assigned to the *trans* form and the other to the *gauche* form:

$$D_t/D_g=\frac{\kappa_t}{2\kappa_g}e^{-\frac{\Delta S}{R}}e^{\frac{\Delta E}{RT}},$$

where $\Delta S=S_g-S_t$ and $\Delta E=E_g-E_t$ denote the differences in entropy and energy, κ the molecular absorption coefficient and suffices t and g refer to the *trans* and *gauche* molecules, respectively. In a narrow range of temperature ΔS and ΔE can be considered to be constant and accordingly the value of ΔE can be determined by measuring the temperature dependence of the ratio D_t/D_g of the two bands. As these bands we have chosen one at 793 cm.$^{-1}$ or 660 cm.$^{-1}$ assigned to the *gauche* form and the other at 743 cm.$^{-1}$ assigned to the *trans* form.* From the measurement in the gaseous state made in the temperature range from 20°C to 150°C, the energy difference has been obtained as:

$$\Delta E=-0.05\pm0.15 \text{ kcal./mol.}$$

For the measurement in the liquid state in the temperature range from 10° to −60°C we have chosen two bands at 789 cm.$^{-1}$ (*gauche*) and at 729 cm.$^{-1}$ (*trans*). The energy difference has been found to be

$$\Delta E=+0.05\pm0.06 \text{ kcal./mol.}$$

This is in agreement with the value obtained by Goubeau and Pajenkamp from their Raman measurement[3], provided that the assignment of lines is made as referred to above.

It is to be noted that the energy difference found in the gaseous state is nearly equal to that in the liquid state. This is compatible with our explanation of the interaction of molecules in the liquid state[8]. It is seen that the *trans* and the *gauche* forms of n-propyl chloride will have almost the same value of the dipole moment which will result in the same change of energy in the liquid state. In other words, the energy difference between the *trans* and *gauche* molecules will have almost the same value in the liquid state as in the gaseous state.

The intensity measurement made for n-propyl bromide by use of two bands at 780 cm.$^{-1}$ (*gauche*) and 658 cm.$^{-1}$ (*trans*) in the temperature range from 20° to 150°C gave the value of enery difference -0.1 ± 0.2 kcal./mol. in the gaseous state.

In our previous papers[4,5,7] we have discussed the energy difference between the *trans* and *gauche* forms of many disubstituted ethanes. The very small value of ΔE

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[7] S. Mizushima, T. Shimanouchi, T. Miyazawa, K. Abe and M. Yasumi, *J. Chem. Phys.*, **19**, 1477 (1951).

* We are sure that no *trans* band (strong enough to disturb the energy difference measurement) overlaps the 793 and 660 cm.$^{-1}$ *gauche* bands, because these two bands disappear in the solid state. Nor is the 743 cm.$^{-1}$ *trans* band considered to be overlapped by any *gauche* band, because the only *gauche* frequency expected to appear in this range is the CH_2-rocking frequency assigned to the 793 cm.$^{-1}$ band. This assignment is made from comparisons with the spectra of n-propyl bromide, dichloroethane, etc. See I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **21**, 2195 (1953).

[8] I. Watanabe, S. Mizushima and Y. Mashiko, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **40**, 425 (1943). See also reference 4).

obtatined for *n*-propyl chloride and bromide is very interesting as compared with the large values found in the cases of 1,2-dichloro and 1,2-dibromoethane. This fact provides us data useful for the further development of our view[5] concerning the nature of the hindering potential to internal rotation**.

Summary

Infrared spectra of *n*-propyl chloride and bromide have been measured in the gaseous, liquid and solid states. The Raman measurement was also made in the liquid state. From the normal vibration calculation and by comparison with the spectra of ethylene chlorhydrin it has been concluded that in the liquid state both the *trans* and *gauche* forms are present and of these only the *trans* form persists in the solid state. The energy difference between the *trans* and the *gauche* forms has been determined by the absorption intensity measurement.

Chemical Laboratory, Faculty of
Science, Tokyo University,
Tokyo

** After our manuscript was finished, a paper by J. K. Brown and N. Sheppard, *Trans. Faraday. Soc.*, 50, 1164 (1954), became available to us. They reported a detailed infrared measurement of *n*-propyl halides in the solid state, the result of which supports our assignment of the bands used for the determination of the energy difference. Other conclusions reported in this paper are also in good agreement with ours.